NEWSLETTER

DIGNAN PHOTOGRAPHIC INC., 12304 ERWIN ST., NO. HOLLYWOOD, CALIF. 91606

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DECEMBER 1969

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EDITORIAL

We would like to take this opportunity to thank you for the hundreds of letters that we received throughout the year that say in essence - "Thank you for making photography more interesting" - We hope you had a very merry Christmas and a wonderful New Year.

ILFORD COLOR NEGATIVE FORMULAS

In this issue, we offer official Ilford Color Negative Formulas. To the best of our knowledge, there are only one or two processing laboratories in this country that possess these formulas.

As we go to press, we have just learned that Ciba of Switzerland has purchased controlling interest in Ilford, Ltd. How this will affect the sale of Ilford products in the United States, we, of course, do not know.

ECO-3

Kodak has a new process called ECO-3 which, we understand, is more compatible with ME-4. So far, we do not have these formulas.

KENDALL ON PHENIDONE

For those of you who feel that the information we offer is not technical enough at times, we are including an article on Phenidone by Kendall of Ilford. Kendall discovered the properties of Phenidone, so we feel that we have gone to "the" authority on this subject. Although this paper was first given in 1953, it still contains enlightening information on this unusual developing agent. We are printing it with the permission of Geigy Industries.

NOTES ON AGFA DUPLICATING FILM

The newer emulsions of Agfa Duplicating Film have a note attached giving the following changes for the developers. The time in the first developer is now listed at 4 minutes. The color developer is now 9 minutes. Use these new times for CT-18 processing. Agfa, evidentally, is now making thinner emulsions.

NEW ITEM

We are now stocking a new 35 mm cassette. These are very easy to load. One end screws on, thus eliminating many of the problems connected with the snap-on type cassettes. Because of the rigid design, you will find these cassettes can be reused dozens of times.

As a special offer to Newsletter subscribers only, we are offering 18 cassettes for $5.00 postpaid.

NO CONTEST WINNERS

We must admit that our contest for Devided Color Developers ended as a complete failure. Although we can announce no winning formulas, we would like to give honorable mention to Robert E. Dunbar, 16 Jameson St., Natick, MA 01760 who did present what we considered a "good try."

* * *

READER'S RIGHT

Question: I have recently received one of your rolls of Fujicolor Print Film #8819. I plan to expose this in my camera, and cannot find any exposure information.
(Al Hermes, 2428 Roosevelt St., Berkeley, CA 94703)

Answer: Print films such as Fujicolor and Agfa Duplicating Film are not listed by the manufacturer as to sensitivity. Each emulsion run is different and the tolerances are much looser than with camera films. As we have previously mentioned, your first roll of Agfa Duplicating Film should be a test to determine the ASA starting at 25 on up to an ASA of around 200. This will give you the exposure index for your film as well as your camera and light meter. Fujicolor Print Film is extremely slow when compared to Agfa Duplicating Film, and we do not recommend it for a camera film. You will probably find it has an ASA of 1 or 2.

Comment:
I have found what I consider to be the best bleach for use with Anscochrome. I found it in a copy of "How to Process Ansco Color Film" by Lars Moen. (ED: This book is no longer in print.) It appears on page 123 and is as follows:

Copper Chloride	500 grams
Water to make	1000 cc

It can also be made from copper sulfate by the addition of salt.

Copper Sulfate	50 grams
Sodium Chloride	50 grams
Water to make	1000 cc

I have never had any difficulty with this bath as opposed to the ferricyanide-bromide formulas. These have sometimes given some degree of frilling, especially in hot weather. Moen also suggests using a double-chloride of copper and ammonia, by adding aqua ammonia to the second bath, but unless one is extremely careful in the addition of ammonia, the gelatin can be lifted very easily from the base.
(Donn Fryant, 519 N. 66th St., Seattle, WA 98103)

Comment:
I have tried the Dupont B & W reversal formula on Panatomic-X at 64 ASA with beautiful results. Using a changing bag, a five gallon water container, and rapid film dryer, I have found this combination great for outdoor photo demonstrations, going from raw film to slide show in 25 minutes.
(Stanley J. Madore, Madore Photo, 74 Monseigneur Langlois Blvd., Pincourt, Quebec, Canada)

Question: We do a considerable amount of underwater photography in color, mostly 8 mm format. To this end, I have built a portable semi-automatic drum processor. The machine driven drum rotates within a "U" bath, which is subsequently surrounded by a controlled water bath usually plugged into hot and cold running water. The water bath is quite large, making for a very stable environment, temperaturewise.

Using this machine, I have tried experimentally on many occasions developing Kodachrome 8 mm (test strips only). My first color development after exposure to red light gives a beautiful cyan color deposit. Subsequent exposure to blue light and development gives the emulsion a green coloring, final exposure to white light generally colors the emulsion reddish (magenta). However, after bleaching and fixing, I end up only with a blue positive.

If you have any words of wisdom or formulas concerning experimental development of Kodachrome, I would much appreciate hearing from you.
(L. H. McCracken, Manager, Island Divers, Ltd., 315A Wesley St., Nanaimo, BC, Canada)

Answer: K-12 is coming soon.

Question: In the February 1969 Newsletter, you have published the official Ansco AR-1 and AR-2 formulas for the processing of the line of Anscochrome films (not the 8 mm movie films), including the duplicating film. In the two schedules on F-133 you set forth the steps, both of which indicate a stabilizing rinse. I've always used this rinse with the kits, but in your formula collection, I do not find this stabilizing rinse set forth. In my search through your Anscochrome Color Formula #6, I found stabilizers listed on page 5 and also on page 10. They differ, and I wonder which, if either, should be used with the official formulas in the Newsletter.

I note also that in the steps for processing the duplicating film, that the stabilizer does not appear. Is there a place for this solution in the duplicating film processing? I can only assume that I can use the same formulas as the other processes - for I have always used them with the duplicating film, including the stabilizer.
(Peter P. Schneider, 10960 S. Prospect Ave., Chicago, IL 60643)

Answer: In Ansco's AR-1 and AR-2, Ansco has discontinued the stabilizer solution. The formaldehyde (which does the stabilizing) is included in the fixer. So, if you decide to do Ansco, the stabilizer bath may be skipped. The time-temperature chart for the duplicating film uses the same chemistry as AR-1 and AR-2.

PLANS FOR THE 8 X 10 SWINGING CANOE

by

Robert K. Fagley

The "Color Canoe Swinger" is meant to be a very simple device to make it easier to use the 8 X 10 Heath-Mitchell Color Canoe.

The device basically provides a fixed axis about which the Canoe can be rotated without having to be concerned about lifting the Canoe out of the temperature control bath or about tilting the Canoe causing the solution to run to one end. The device permits the Canoe to be rotated and controlled with just one hand, leaving the other hand free to manipulate the wash-water hose or to be ready with the next solution.

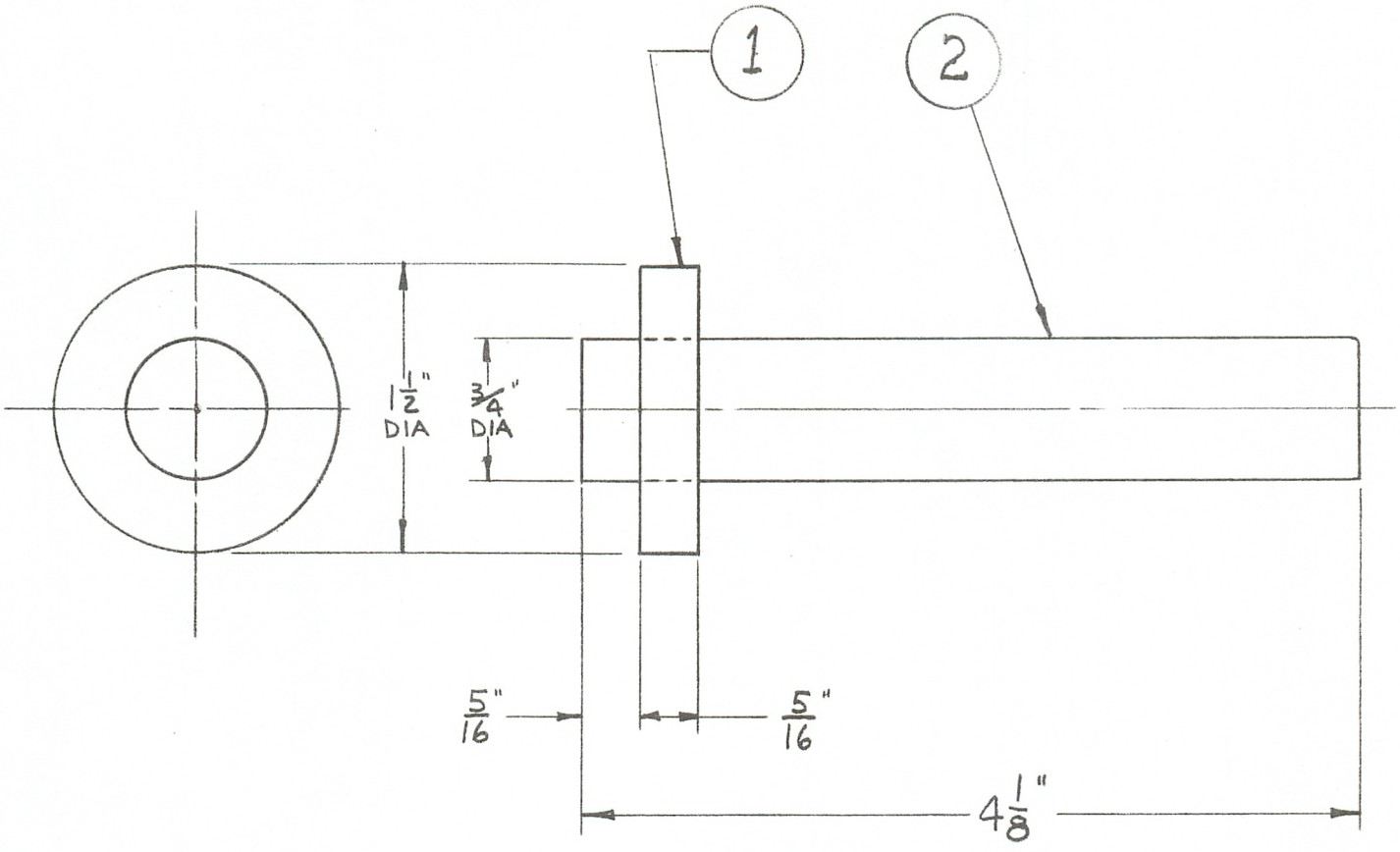
Four sketches are enclosed. The sketches of the Trunnion and the Support are to scale, full size; which fact permits them to be used as patterns. Glue these two sketches to a stiff piece of cardboard with rubber cement. Cut around the outline of the two notches in the Supports. Do not cut out for the holes in the patterns. The patterns can now be used to trace around to mark the shape of the parts on the 5/16" plastic for the two Supports and on the 1" plywood for the two Trunnions. On the plastic, either use a sharp pointed instrument to mark around the pattern, or roughen the surface with sandpaper to allow it to take pencil. Cut the parts out leaving some margin for sanding to size. Sand the parts to size. A 1/8" dia. round file is handy for filing the notches in the Supports to size. Use extreme caution in filing these notches because they are required to support the Canoe. If they are made too large, the Canoe will be wobbly. Punch through the patterns at the hole locations with a sharp pointed tool to mark the hole centers on the parts.

Because the 3/4" dia. holes in the Trunnions and in the Supports are required to be close fits, it is suggested that you obtain at least two 3/4" bits designed for use in power drills (spade bits). These bits have two cutting edges which you can file or grind to reduce the size of the hole if required. The 3/4" dia. holes in the Supports should be free fitting on the 3/4" plastic rod, but not so loose that you can rattle the shaft around in the hole. The 3/4" dia. hole in one of the Trunnions should be a very tight fit on the rod, while the hole in the other trunnion should allow the rod to be moved in and out freely. These various fits can be obtained by first drilling holes in scrap material and then grinding or filing a little off the cutting edges of the bit to reduce the size of the hole as necessary to obtain the desired fit. If a hole is a little on the small side, wrap a piece of sand paper around a wood dowel slightly smaller than the hole and sand the inside of the hole to the proper fit. In drilling

the holes, drill from one side until the center of the bit pokes through the other side. Then finish drilling the hole from the other side. The axis of the holes in the Trunnions especially should be as close to being perpendicular to the surface of the piece as possible. Drill the wash-water-hose hole in the Trunnion which has the tight-fitting hole. This hole should be a snug fit on the hose you will be using, so the hose will stay in place when the wash water is turned on.

Make the two Support Shaft Assemblies, following the sketch. When gluing the Stop Washers to the Shafts, make sure the face of the Washer is as close to being perpendicular to the axis of the Shaft as possible.

Cut the Base out of 1" plywood to the dimensions shown on the Assembly Sketch. To attach the Trunnions to the Base, first drill clearance holes in the Trunnions. Line up the Trunnions using a dowel through the 3/4" holes as shown in the Sketch. Tack the Trunnions in place with finishing nails temporarily. Now, using the holes previously drilled in the Trunnions as a guide, drill smaller pilot holes into the edge of the Base. Pull off the Trunnions and remove the finishing nails. Re-assemble the Trunnions to the Base using the specified screws. If you prefer to have the Trunnions permanently attached, apply waterproof glue to the mating surfaces before tightening up the screws. Apply 3 or 4 coats of a waterproof finish to all surfaces of the wood parts.



(1) STOP WASHER - ¾" I.D. X 1½" O.D. X 5/16" THK. ACRYLIC PLASTIC.

(2) SUPPORT SHAFT- ¾" DIA. X 4⅛" LG. ACRYLIC PLASTIC.

GLUE (1) TO (2) USING ACRYLIC CEMENT.

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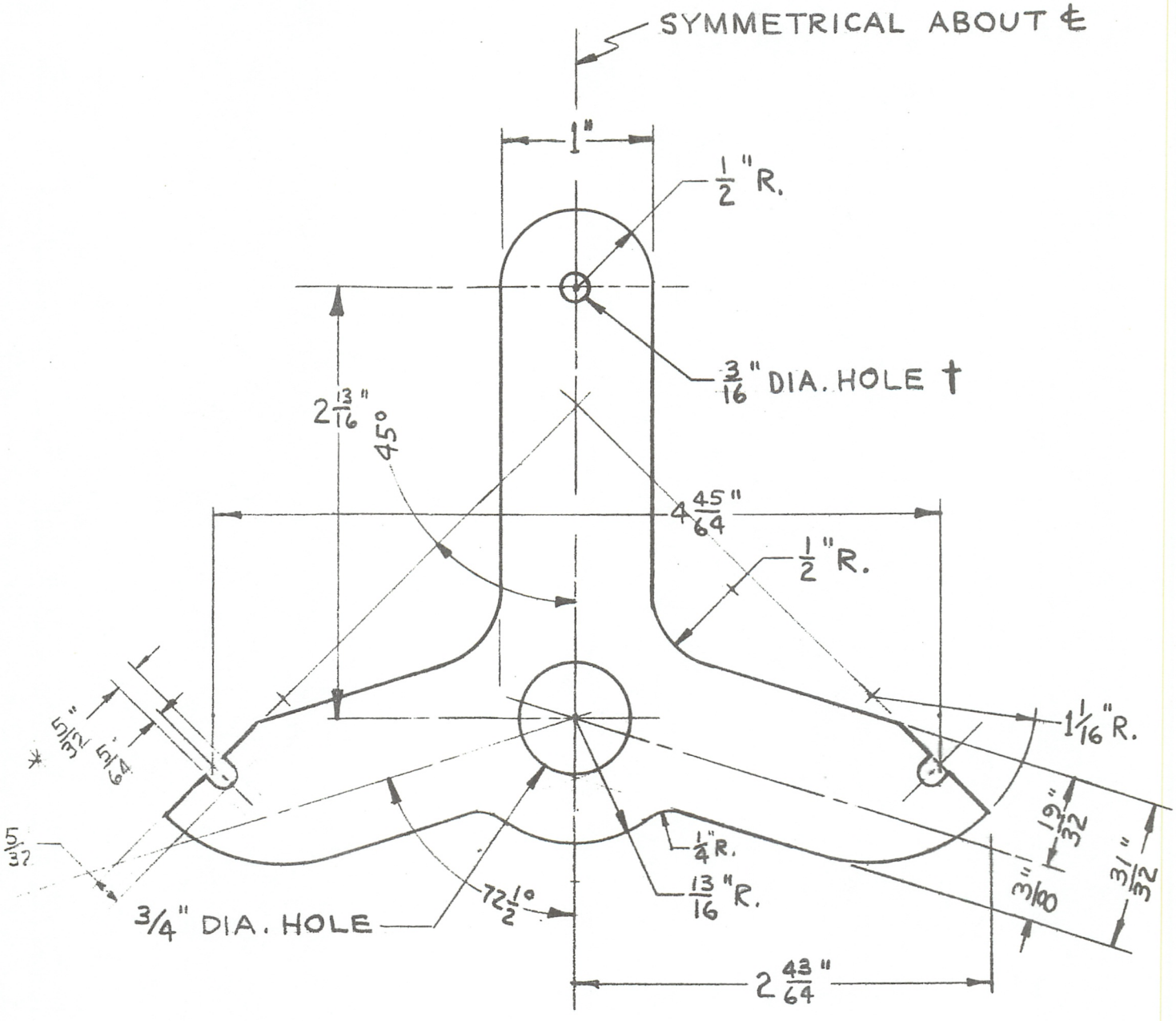
COLOR CANOE SWINGER
CANOE SUPPORT SHAFT ASSY.

R. K. Fogley - 12 NOV. '69



* NOTCHES SHOULD BE FILED TO FIT LIPS OF COLOR CANOE USED. PREFERABLY, MAKE ENTIRE PART FROM 1/4" HARDBOARD FIRST TO OBTAIN CORRECT FIT.

† HOLE FOR ATTACHING COUNTERWEIGHTS. FOR WEIGHTS, USE STEEL WASHERS OR LEAD CUT FROM LEAD INGOT (FROM PLUMBING SUPPLY STORE) OR FROM LEAD SHEET. EACH WEIGHT SHOULD WEIGH ABOUT 8 OZ.

MAT'L: 5/16" THICK ACRYLIC PLASTIC.

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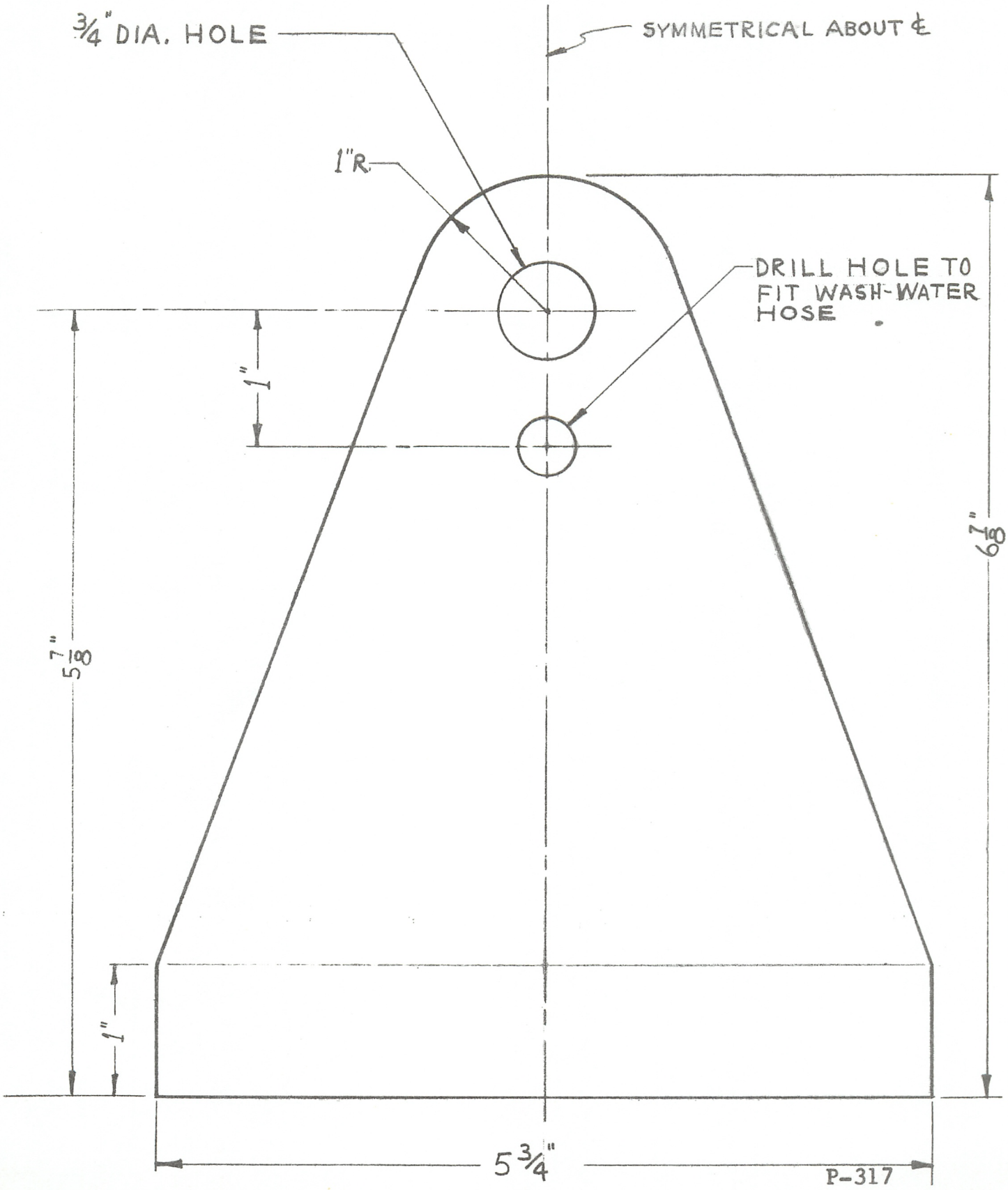
COLOR CANOE SWINGER
CANOE SUPPORT

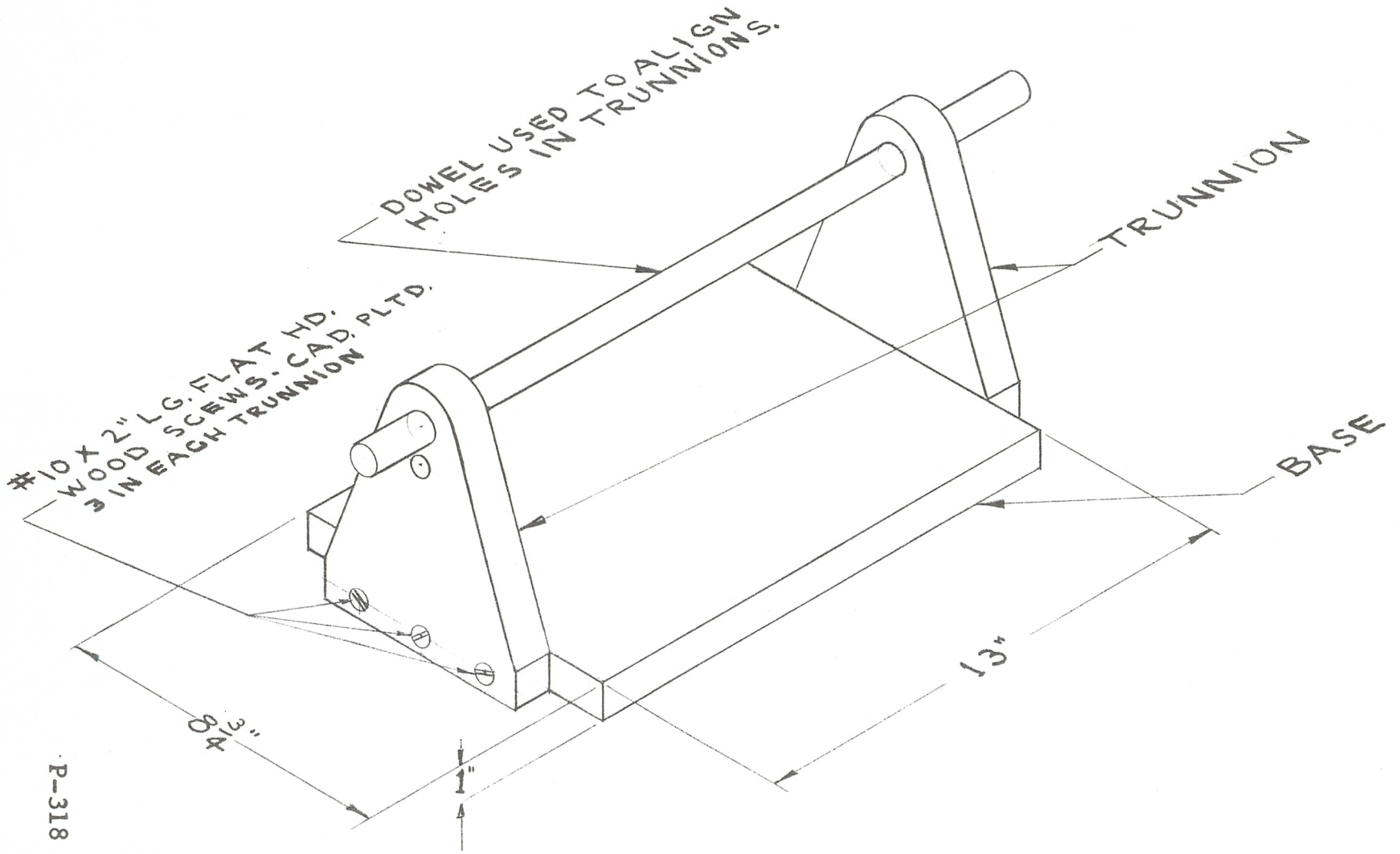
R.K. Fogley - 12 NOV. '69



SUGGESTED MAT'L - 1" THICK PLYWOOD

COLOR CANOE SWINGER
CANOE SUPPORT TRUNNION

R.K. Fagley - 12 NOV. '69



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COLOR CANOE SWINGER
ASSEMBLY OF WOOD PARTS

R.K. Fagley 12 NOV. '69

Phenidone—The Mechanism of its Developing Action and its Super-additivity with Hydroquinone*

A. J. AXFORD and J. D. KENDALL

Research Laboratories, Ilford Ltd.

ABSTRACT. A study has been made of the photographic behaviour of Phenidone and selected series of Phenidone-hydroquinone (PQ) developers, and their properties compared with those of analogous MQ developers. The results demonstrate the greater super-additivity of the PQ developing system, and have some bearing on current theories of development. Other experimental work on certain aspects of the chemistry of Phenidone shows that no sulphonation of the Phenidone takes place during development in the presence of sulphite. A mechanism for the PQ developing system is postulated which involves a coloured reversible mesomeric free-radical formed by the loss of an electron from the pyrazolidone ion.

INTRODUCTION

THE developing action of Phenidone† (1-phenyl-3-pyrazolidone) and its ability to activate hydroquinone was first discovered in 1940[1]. Chemically the structure of Phenidone is completely unlike that of any of the previously known types of organic developing agents, so that the reasons for its photographic properties are not obvious. It is the object of this paper to describe some investigations into the developing properties of Phenidone and of Phenidone/Hydroquinone (PQ) combinations, to postulate a mechanism for the action of these systems and to indicate the bearing the experimental results have on current theories of development.

During the course of these investigations a study was made of the photographic behaviour of selected series of PQ and MQ developers (Section A—Part I). The results clearly demonstrate the marked super-additivity of the PQ developing system and enable a direct comparison to be made with that of the MQ system.

Other experimental work described covers a preliminary study of certain aspects of the chemistry and mechanism of the photographic action of Phenidone (Section A—Part II), with results which are relevant to the theoretical discussion (Section B).

SECTION A

Part I.—The Super-Additivity of Phenidone with Hydroquinone

Several series of developers were prepared in which, although the ratios of the organic reducing agents were varied, the total molar concentration of these agents in a given series remained constant, and the sulphite and restrainers unchanged. For each series the *p*H was adjusted to a previously selected value.

From the study of those developers in which Phenidone constitutes 100 per cent of the total molar concentration of organic reducing agents, information is obtained concerning the photographic properties of Phenidone when used as the sole developing agent. The behaviour of a developer, selected from one of the PQ series for its similarity to the reference MQ developer, when compared with that of this reference by means of graphs, illustrates also the superior resistance to exhaustion of the PQ developing system.

Variants and Criteria

(*a*) *Selected Reference Developer*—The Ilford developer I.D.2, the stock solution formula of which is given below, is a typical MQ negative developer with good photographic properties.

Metol	2 *gm.* (=1.16 *centimoles*)
Na_2SO_3 (*anhydrous*)	75 *gm.*
Hydroquinone	8 *gm.* (=7.27 *centimoles*)
Na_2CO_3 (*anhydrous*)	37.5 *gm.*
KBr	2 *gm.*
Water	*to* 1 *litre*

A dilution of 1+2 with water provides a dish-strength developer in which the total molar concentration of organic agents is 2.81 centimoles per litre, and the percentage molar concentration of metol is 13.75 per cent.

In the Phenidone/Hydroquinone series (except for a considerable reduction in the carbonate for the developers at the lower *p*H) the "salts" in the above formula were unchanged, but the total molar concentration of organic

*Read to the International Conference on the Science and Application of Photography, organized by The Royal Photographic Society, London September 1953.

†Registered Trade Mark of Ilford Ltd.

Table I

Developer Reference	MQ/A	MQ/B	MQ/C*	MQ/D	MQ/E	MQ/F	MQ/G
Molar % Metol	0	5	13.75	25	40	70	100
Molar % Hydroquinone	100	95	86.25	75	60	30	0

*I.D.2—Dish Strength

agents was reduced by 12 per cent from 2.81 to 2.496 centimoles per litre. This reduction is consequent upon the arbitrary replacement of the metol in I.D.2 by one sixth of its weight of Phenidone, i.e. 0.33 gm. per litre in the stock, this fractional substitution being dictated by experience.

Whilst this change in molar concentrations necessitates caution when making comparisons between the MQ and PQ series, it does not influence arguments on the super-additivities of the different systems.

(*b*) *Processing Conditions*—Dish development with continuous systematic lateral rocking was employed for this work. Brushing was avoided because of the possibility, discussed later, of inhibiting effects due to developer oxidation by-products.

The baths were adjusted to 68°F. immediately before the commencement of processing and the temperatures rechecked on completion.

Ilford HP3 sheet film was exposed through a step wedge with a log exposure increment of 0.25. These strips were processed always on the day the exposures were made.

Six strips were developed simultaneously and were removed from the developer at intervals of 1, 2, 4, 7, 11, and 16 minutes, immersed immediately in 30 per cent acid hardening hypo for ten minutes, and finally washed for 30 minutes in each case.

(*c*) *Sensitometric Criteria.*—In order to avoid the introduction of factors unnecessary for the present purpose we have considered development to a value $\overline{G}=0.7$. $\overline{G}$ may be defined as the average slope between two points on the characteristic curve, the first point being the log E value at 0.10 above fog (i.e., $S_{0\cdot1}$) and the second the log E value at $(S_{0\cdot1}+1.5)$. This was considered to be an average condition for the high-speed negative emulsion employed, since this term reflects to some extent not only the contrast but the shape of the foot of the characteristic curve. The relative foot-speed was measured at a density of 0.1 above fog.

The sensitometric data from each of the 70 developers considered here has provided the conventional plottings of $\overline{G}$ (log E 1.5) against time, $S_{0\cdot1}$ against time and fog against time. The time at which the $\overline{G}$ first reaches 0.7 has been considered for those cases where fog growth causes a second appearance of this contrast.

(*d*) *Control of* p*H.*—The corrected *p*H of Ilford I.D.2 at dish strength is 10.36. Every developer in the MQ series, and the PQ series operating at the higher *p*H, was adjusted to this *p*H exactly by the addition of 10 per cent NaOH solution or 5 per cent H_2SO_4. Each member of the PQ series working at the lower *p*H of 9.8 was adjusted by the addition of 10 per cent Na_2CO_3 solution to the modified formula.

(*e*) *Variations in the Constitutions of the Developers.*

(i) *Metol/Hydroquinone series.*—Developers of differing molar ratios were compounded (Table I) by the simple process of mixing suitable proportions of solutions of equal molar concentrations containing either metol or hydroquinone so that the total molar concentration was maintained at 2.81 centimoles per litre.

These seven ratios proved adequate for the MQ series.

(ii) *Phenidone/Hydroquinone series.*—The possibility that slight aerial oxidation might change the character of those developers which contained very low proportions of Phenidone precluded the employment of the two-stock-solution method for the preparation of these series, and each PQ developer was compounded separately. The number of developers per series also was increased appreciably in order to indicate clearly the rapid changes in activity with the change in Phenidone at low concentrations (Table II). The total molar concentration of developing agents was maintained at 2.496 centimoles per litre in each case.

Four series of developers were compounded with the above ratios of agents; Series I at *p*H 10.36, Series II at *p*H 9.8 (by reduction in the carbonate content), Series III as Series I but containing, as an additional restrainer, one part of benzotriazole per 20,000 of working solution, and Series IV as Series II but with a similar quantity of benzotriazole.

By plotting the times taken to reach a $\overline{G}$ (log E 1.5) of 0.7 against the percentage molar compositions of the developers, it is possible to demonstrate and compare the super-additive actions in MQ and PQ systems. The relative foot-speeds at this contrast can be compared by similar means.

Table II

Developer Reference	PA	PB	PC	PD	PE	PF	PG	PH	PI	PJ	PK	PL	PM	PN	PO
Molar % Phenidone . . .	0	0.5	1	2	4	7	11	16	25	40	60	70	80	90	100
Molar % Hydroquinone . .	100	99.5	99	98	96	93	89	84	75	60	40	30	20	10	0

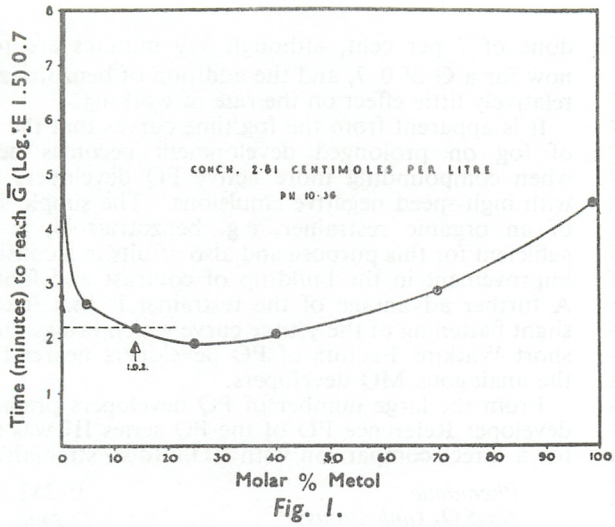


Fig. 1.

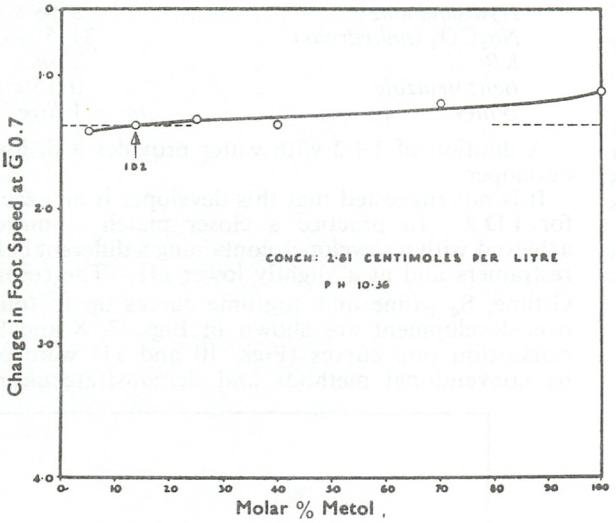


Fig. 2.

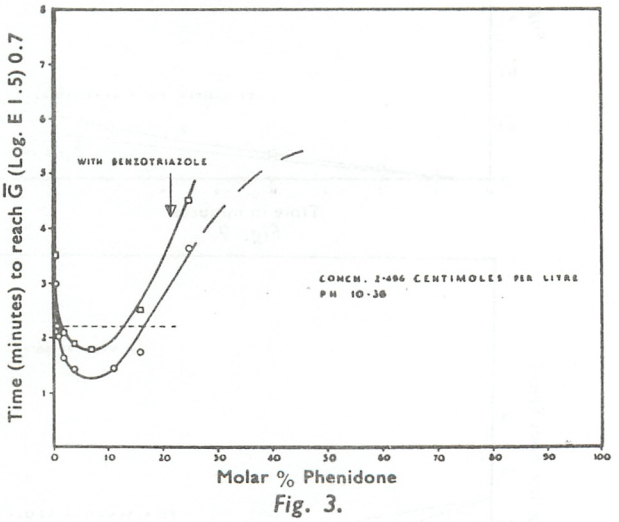


Fig. 3.

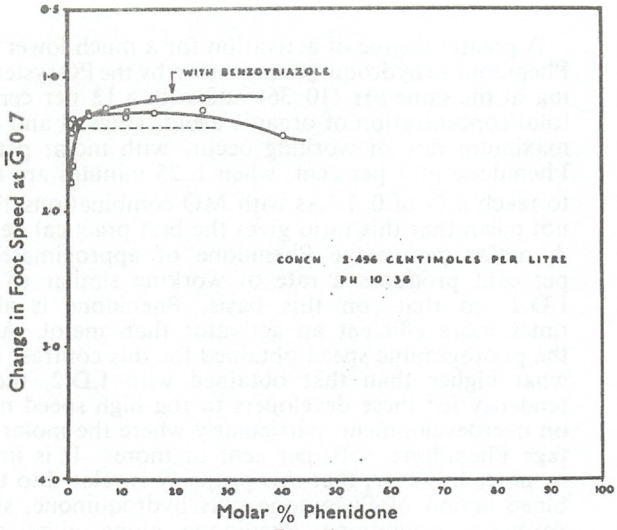


Fig. 4.

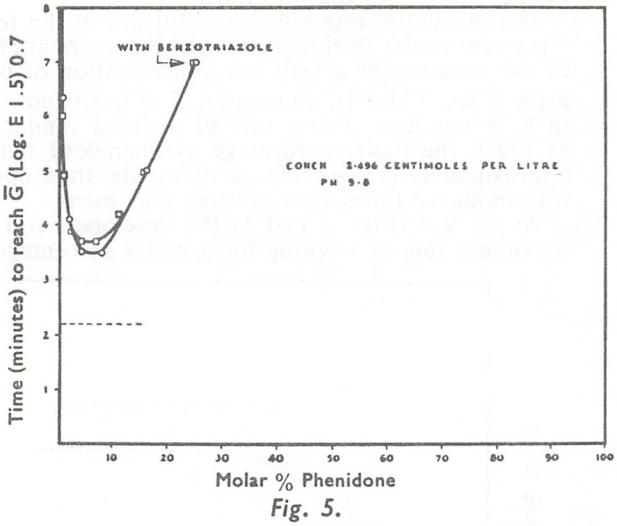


Fig. 5.

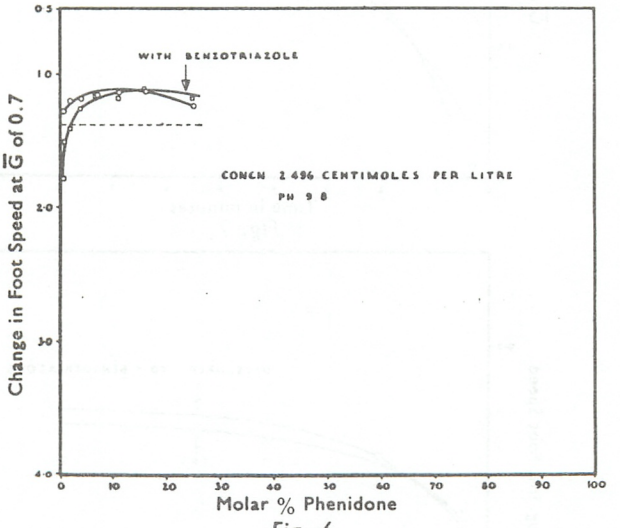


Fig. 6.

Results

The maximum rate of working for the MQ series of developers (Figs. 1 and 2) is obtained with a molar percentage metol of 28 per cent, 1.9 minutes being required to reach $\overline{G}$ 0.7. When the molar percentage metol is 13.75 per cent, i.e. I.D.2 (dish strength), the time required is 2.2 minutes, but this ratio of metol to hydroquinone, whilst not the most rapidly working, gives in practice a developer with good general photographic characteristics, particularly with regard to the growth of fog on prolonged development. In this series the relative foot-speed and fog at $\overline{G}$ 0.7 increase steadily as the molar percentage metol rises.

A greater degree of activation for a much lower ratio of Phenidone to hydroquinone is shown by the PQ system working at the same *p*H (10.36) and with a 12 per cent lower total concentration of organic agents (Figs. 3 and 4). The maximum rate of working occurs with molar percentage Phenidone of 7 per cent, when 1.25 minutes are required to reach a $\overline{G}$ of 0.7. As with MQ combinations this does not mean that this ratio gives the best practical developer. A molar percentage Phenidone of approximately 0.75 per cent produces a rate of working similar to that of I.D.2, so that, on this basis, Phenidone is about 18 times more efficient an activator than metol. Although the photographic speed obtained for this contrast is somewhat higher than that obtained with I.D.2, there is a tendency for these developers to fog high speed materials on overdevelopment, particularly where the molar percentage Phenidone is 10 per cent or more. It is important to note, however, that this property is related to the combined action of Phenidone plus hydroquinone, since the developer containing Phenidone alone gives a much smaller increase of fog with time.

The maximum rate efficiency still lies in the region of 7 per cent molar Phenidone for the PQ series at *p*H 10.36 in the presence of a very low concentration of benzotriazole (Figs. 3 and 4), although a $\overline{G}$ of 0.7 is now reached in 1.75 minutes. For a rate of working similar to that of I.D.2, the molar percentage of Phenidone required is approximately 1.3 per cent, so that under these conditions it is about ten times more efficient than metol.

At *p*H 9.8 (Figs. 5 and 6) PQ developers still show a maximum rate of working for a molar percentage Phenidone of 7 per cent, although 3.9 minutes are required now for a $\overline{G}$ of 0.7, and the addition of benzotriazole has relatively little effect on the rate of working.

It is apparent from the fog/time curves that the control of fog on prolonged development becomes necessary when compounding more active PQ developers for use with high-speed negative emulsions. The simple addition of an organic restrainer, e.g. benzotriazole, is usually sufficient for this purpose and also results in a considerable improvement in the build-up of contrast and foot-speed. A further advantage of the restrainer is that it causes a slight flattening of the γ/time curve which brings the rather short Watkins Factors of PQ developers nearer those of the analogous MQ developers.

From the large number of PQ developers prepared the developer Reference PD of the PQ series III was selected for a direct comparison with I.D.2 (dish strength).

Phenidone	. . . . .	0.242 *gm.*
Na_2SO_3 *(anhydrous)*	. . .	75 *gm.*
Hydroquinone	. . . .	8.08 *gm.*
Na_2CO_3 *(anhydrous)*	. . .	37.5 *gm.*
KBr	. . . . .	2 *gm.*
Benzotriazole	. . . .	0.15 *gm.*
Water	. . . . *to*	1 *litre*

A dilution of 1+2 with water provides a dish-strength developer.

It is not suggested that this developer is an exact match for I.D.2. In practice a closer match is more easily achieved with a developer containing a different balance of restrainers and at a slightly lower *p*H. The comparative $\overline{G}$/time, $S_{0.1}$/time and fog/time curves up to four times over-development are shown in Figs. 7, 8 and 9. The exhaustion rate curves (Figs. 10 and 11) were obtained by conventional methods and demonstrate clearly that

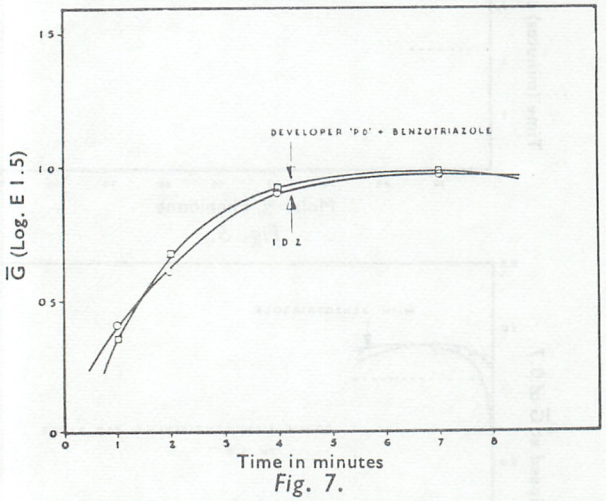


Fig. 7.

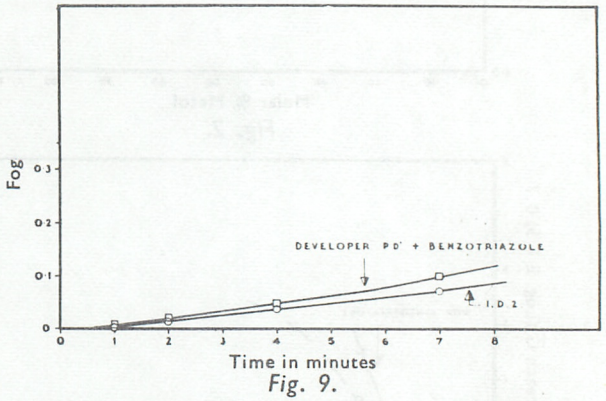


Fig. 9.

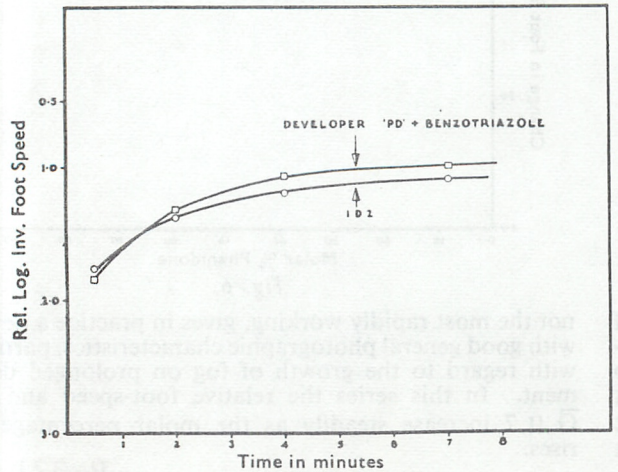
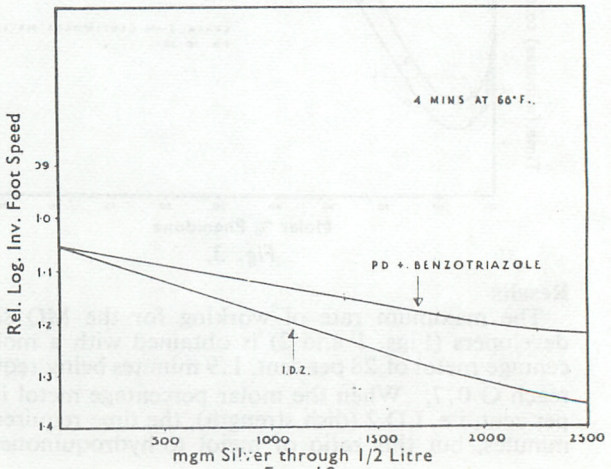


Fig. 8.



F . 10.

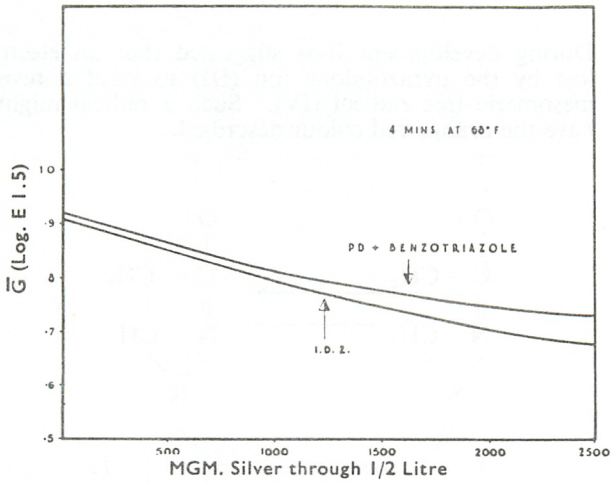


Fig. 11.

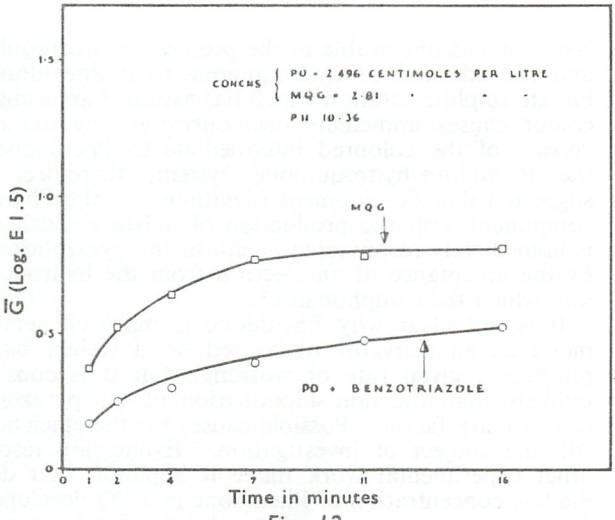


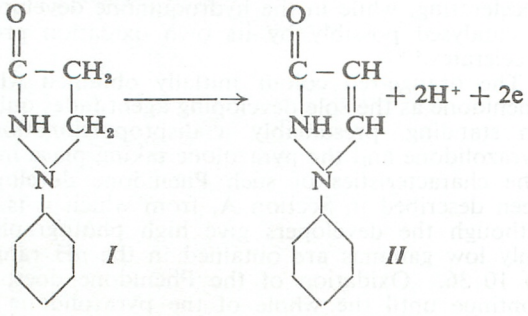
Fig. 12.

even with a 12 per cent lower total concentration of organic agents in the PQ developer it maintains its foot-speed better than I.D.2.

Phenidone developers, without hydroquinone, can be employed for the production of very high photographic speed at rather low contrasts. The comparative characteristics of developers References PO and MQ/G, which contain Phenidone alone and metol alone respectively, are shown in Figs. 12, 13 and 14.

Part II. The Chemistry and Mechanism of Developing Systems employing Phenidone

The oxidation of an alkaline solution of 1-phenyl-3-pyrazolidone (I) normally results in the production of the corresponding 1-phenyl-3-pyrazolone (II), which is completely inert photographically.



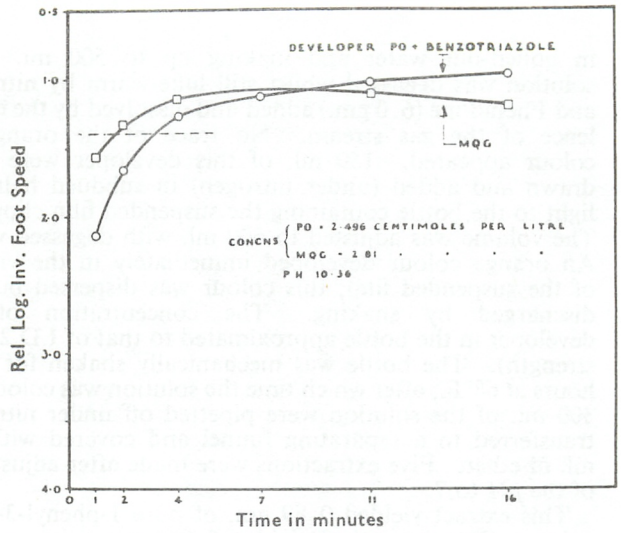


Fig. 13.

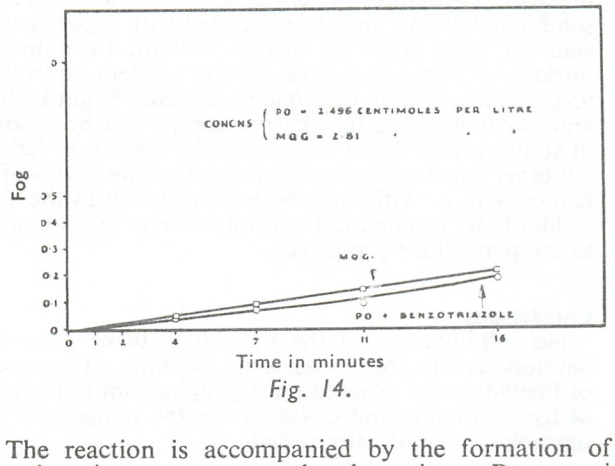


Fig. 14.

The reaction is accompanied by the formation of a transient intense orange-red colouration. Regeneration of the pyrazolidone by the reduction of the pyrazolone can be achieved only by extreme conditions. Under photographic conditions such a reduction is not possible since the pyrazolone is unaffected by hydroquinone.

Experiments were carried out to determine whether (i) the oxidation of an alkaline solution of Phenidone by silver bromide in the presence of sodium sulphite is accompanied by any sulphonation.

(ii) The presence of gelatin and excess bromide ions have any influence on the results, and

(iii) The oxidation of a normal Phenidone developer by photographic film gives quantitatively the pyrazolone.

The progress of the reaction in the total absence of atmospheric oxygen was also investigated.

The results of these experiments show that the course of reaction is the same in each case and only (iii) need therefore be discussed in detail.

Experimental Procedure (iii)

The process was carried out in a glass bottle of 650 ml. capacity, graduated at 600 ml. 150 gm. of HP3 film clippings (coating weight 36 mgm. Ag per gm.) were suspended in approximately 300 ml. of boiled water and this slurry degassed by a stream of nitrogen. An air free developer was compounded by dissolving

Sodium sulphite, anhydrous . .	37.5 *gm.*
Sodium carbonate, anhydrous .	18.75 *gm.*
Potassium bromide . . .	0.1 *gm.*

in boiled-out water and making up to 500 ml. This solution was degassed whilst still luke-warm by nitrogen, and Phenidone (6.0 gm.) added and dissolved by the turbulence of the gas stream. No trace of the orange-red colour appeared. 150 ml. of this developer were withdrawn and added (under nitrogen) in subdued half-watt light to the bottle containing the suspended film clippings. The volume was adjusted to 600 ml. with degassed water. An orange colour developed immediately in the vicinity of the suspended film; this colour was dispersed but not discharged by shaking. The concentration of the developer in the bottle approximated to that of I.D.2 (dish strength). The bottle was mechanically shaken for three hours at 68°F., after which time the solution was colourless. 300 ml. of the solution were pipetted off under nitrogen, transferred to a separating funnel and covered with 150 ml. of ether. Five extractions were made after adjustment of the *p*H to 7.

This extract yielded 0.89 gm. of pure 1-phenyl-3-pyrazolone. The theoretical yield is 0.889 gm.

After stopping development in the bottle by the addition of excess bisulphite, the clippings were washed free from soluble halide ion and then digested with 5 per cent nitric acid for four hours at 40°C. Volhard titration of the nitric acid suspension gave a silver content equivalent to 95 per cent of the pyrazolone produced. Slight hydrolysis and swelling of the film base accompanied by absorption of solution is believed to account for the silver deficiency. All other experiments conducted with suspensions of silver halide, with or without gelatin present, but in the absence of film base, resulted in the production of silver equivalent to the pyrazolone produced.

Conclusions

No sulphonation of the Phenidone takes place during development in the presence of sulphite. The oxidation of Phenidone by exposed photographic film in the absence of hydroquinone and oxygen gives the pyrazolone via an unstable coloured intermediate.

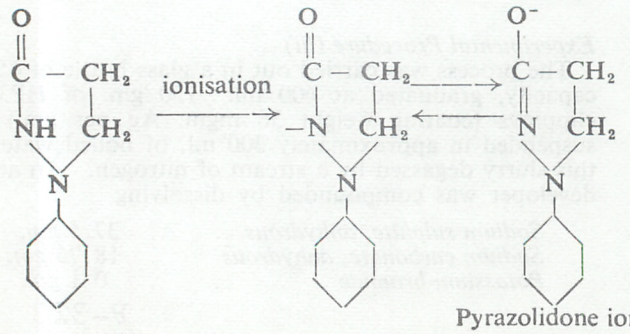
SECTION B

The Mechanism and Super-Additive Behaviour of the Phenidone/Hydroquinone Developing System

It has been established that when used as the sole developing agent 1-phenyl-3-pyrazolidone is oxidised to the pyrazolone via an unstable coloured intermediate. The constitution of this coloured intermediate is indefinite, but other investigations which are still in progress favour a free-radical mechanism for development processes involving Phenidone. The fundamental development requires the acceptance of an electron by the silver halide.

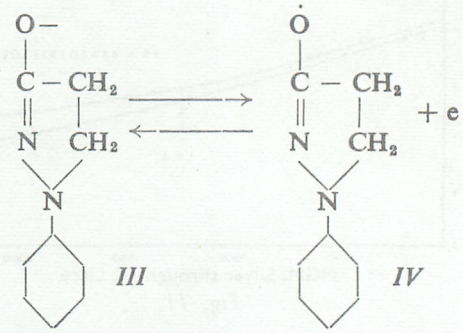
$$AgBr + e \longrightarrow Ag + Br^-$$

Phenidone shows no apparent keto-enol tautomerism and its acidic properties are due rather to a lactam-lactim system



Pyrazolidone ion

During development it is suggested that an electron is lost by the pyrazolidone ion (III) to yield a reversible mesomeric free radical (IV). Such a radical might well have the orange-red colour described.



III *IV*

No colour is observable in the presence of hydroquinone, and the addition of hydroquinone to a Phenidone/carbonate/sulphite solution which has assumed an orange-red colour causes immediate decolourization by the reconversion of the coloured intermediate to Phenidone. In the Phenidone/hydroquinone system, therefore, it is suggested that development is initiated by the Phenidone component with the production of a free radical, which is immediately reconverted *in situ* to the pyrazolidone ion by the acceptance of an electron from the hydroquinone ion, which then sulphonates.[2]

It is not clear why Phenidone is more efficient than metol as an activator (measured on a weight basis to produce a given rate of working), but it is considered unlikely than the non-sulphonation of the pyrazolidone is a primary factor. Possible causes for the efficiency are still the subject of investigation. Exhaustion tests and other experimental work make it apparent that despite the low concentration of Phenidone in a PQ developer the former remains at a constant value until a large part of the hydroquinone has been consumed. If a highly efficient regenerative process is assumed, the fact that the pyrazolidone is not lost by sulphonation might be one reason why the PQ system does not exhaust as rapidly as the MQ system in which there appears to be a slight but continuous loss of metol by sulphonation.[3]

The induction period of the developer Reference PD is about 25 seconds, whilst that of a simple Phenidone developer of the same molarity approaches zero. On the other hand, a developer containing only the Phenidone component of developer PD has an induction period of 30 to 35 seconds, whilst that of a developer with only the hydroquinone component is four minutes. It would appear therefore that the induction period of aPQ developer is related to the very low ionic concentration of Phenidone at the liquid/crystal interface. In addition, the rate of image growth in the Phenidone-component developer is decelerating, while in the hydroquinone developer, which is catalysed possibly by its own oxidation products, it accelerates.[4,5]

The orange-red colour initially obtained when using Phenidone as the sole developing agent fades quite rapidly on standing, presumably a disproportionation to the pyrazolidone and the pyrazolone taking place in solution. The characteristics of such Phenidone developers have been described in Section A, from which it is seen that although the developers give high photographic speed, only low gammas are obtained in the *p*H range of 8.2 to 10.36. Oxidation of the Phenidone does, however, continue until the whole of the pyrazolidone has been converted to the pyrazolone. The reason why Phenidone

has these photographic properties is not clear, but it is possible that the initially rapid developing action is inhibited by a primary oxidation product which is reducible by hydroquinone.

At a *p*H of 8.2 where a simple hydroquinone developer shows negligible photographic activity, a PQ developer in which the molar percentage Phenidone is 2 per cent, is more active than a developer of the same total molarity containing Phenidone only. It is significant that even at this *p*H the orange-red colour formed from the Phenidone is instantly discharged by hydroquinone. Since at this *p*H the concentration of the bivalent hydroquinone ion is negligible, it can be assumed that the activity of a PQ developer at a low *p*H is due solely to the action of uninhibited Phenidone.

At higher alkalinities (*p*H 10—10.5) experimental evidence suggests that the hydroquinone makes a major contribution to development (although this is clearly facilitated by the presence of the pyrazolidone) and this does not agree with a purely regenerative process. Thus, working in this *p*H range it is possible to compound PQ developers which have characteristics similar to those of high contrast hydroquinone/caustic types at a much higher *p*H.

Aminophenols also discharge the orange-red colour obtained initially with Phenidone developers, but whilst Phenidone/metol developers exhibit a form of superadditivity, their characteristics in the *p*H range 10—10.5 are very different from those of corresponding PQ developers at the same *p*H. These differences should not occur if both the hydroquinone and metol acted merely as regenerating agents. At the higher *p*H values, therefore, it is likely that after the charge barrier has been penetrated by the pyrazolidone ion and the development centre enlarged, the hydroquinone in a PQ system is able to assume an independent active rôle.[6]

Acknowledgments

The authors wish to thank the Directors of Ilford Limited for permission to publish this work, and Dr. G. F. Duffin for his invaluable assistance with the synthesis of Phenidone and his contributions to the discussions on the mechanism of its action. Thanks are due also to Mr. D. J. Fry for helpful criticism, and other members of the staff of Ilford Limited for assistance with much of the experimental work.

References

(1) Kendall, J. D., *B.P.*, 542, 502.
(2) *cf.* Tausch, E., *Zur Chemie der photographischen Entwickler*, Thesis —Berlin, 1934.
(3) *cf.* Levenson, G. I. P., *Phot. J.*, 92B, 109, 1952.
cf. Levenson, G. I. P., *Phot. J.*, 89B, 13, 1949.
(4) Staude, H., *Z. wiss. Phot.*, 38, 65, 1939.
(5) James, T. H., *J. Franklin Inst.*, 240, 327, 1945.
(6) *cf.* James, T. H., *J. Phot. Soc. Am.*, 9, 62, 1943.

ILFORD COLOR NEGATIVE FILM PROCESSING FORMULAS

Preparation of Solutions

To make up each bath, dissolve in water at 68° to 95°F. (20° to 35°C.) the contents of the packages in alphabetical order. For Ilford Color Negative Film Developer and Replenisher, dissolve in approximately nine-tenths of the total volume, for the remaining solutions approximately three-quarters of the total volume. As soon as the chemicals have dissolved, make up to the final volume with water. In some hard water areas, it may be preferable to use distilled or demineralized water.

Solution Life

If solutions are left in processing tanks, floating lids must be used. Otherwise solutions should be returned to well stoppered containers when not in use. Without replenishment, Ilford Color Negative Film Developer will keep under these conditions for at least two weeks and the remaining solutions at least two months.

Solution Capacity Without Replenishment

When using Ilford Color Negative processing solutions without replenishment, not more than 20 120/620 films should be processed per one U. S. gallon (3.8 liters, 0.8 Imperial gallon).

Process Control

With tank processing agitation should be given initially by fully lifting twice and re-immersing, then subsequently by lifting and re-immersing once every 20 seconds. Alternatively, any other system of agitation, such as that provided by nitrogen burst equipment, which is capable of giving the same degree and uniformity of agitation, may be used. Nitrogen burst agitation is not recommended when spiral film holders are used.

At the end of each stage, 10 seconds drainage should be given before proceeding to the subsequent stage. The final wash (Stage 9) may be reduced to a minimum of 3 minutes if the surface wetting of films is unsatisfactory. The conditions of drying should be such that films are dried within 2 hours. Over drying should be avoided.

Notes On Proprietary Chemicals

Antifoam RD	Methylpolysiloxane antifoaming agent (available from Ilford Limited)
Color Developing Agent MI 166	4-animo-N-ethyl-N-(4-hydroxybutyl)-aniline sulphate (available from Ilford Limited) We would suggest DD-8 as a substitute 1:1
Lissapol	Polyethylene glycol

ILFORD COLOR NEGATIVE FILM PROCESSING FORMULAS

PROCESSING PROCEDURE

Light	Step	Solution	Time	Temperature
Total Darkness	1.	Developer (RCD27)	6 min.	75° ± ½°f.
	2.	Stop (F-16)	4 min.	77° - 77°f.
	3.	Wash	4 min.	" "
	4.	Bleach (B9)	4 min.	" "
	5.	Wash	4 min.	" "
Room Lighting	6.	Fix (F-5)	4 min.	" "
	7.	Wash	4 min.	" "
	8.	Conditioner (C-1)	4 min.	" "
	9.	Wash	4 min.	78° - 77°f.
	10.	Dry		Preferably not more than 110°f.

COLOR DEVELOPER RCD27

			Dignan Cat. No.
Distilled or softened water	800.0	cc	
Sodium Metaborate	53.3	grams	S-700
Sodium Hydroxide	2.0	grams	**
Sodium Sulfite (anhy.)	3.9	grams	S-900
Potassium Bromide	0.70	grams	P-530
Hydroxylamine Sulfate	2.34	grams	H-650
Sodium Sulfate (anhy.)	7.8	grams	S-770
M1166	6.0	grams	**
Antifoam RD	0.25	cc	**
Distilled or softened water to	1.0	liter	

pH: average pH at 77°f is 10.50. Formulations which have a measured pH outside the range 10.28 - 10.72 should not be taken into use. Accepted formulations should be pH adjusted to 10.50 ± 0.10, using 2N sulfuric acid or 2N sodium hydroxide solution before being taken into use.

**Not carried by Dignan Photographic, Inc.

ILFORD NEGATIVE FILM
PROCESSING FORMULAS

REPLENISHER R14 FOR COLOR DEVELOPER RCD27

			Dignan Catalog Number
Distilled or softened water	800.0	cc	
Sodium Metaborate	57.0	grams	S-700
Sodium Hydroxide	4.0	grams	**
Potassium Bromide	0.35	grams	P-530
Sodium Sulfite (anhy.)	4.5	grams	S-900
Hydroxylamine Sulfate	3.4	grams	H-650
Sodium Sulfate (anhy.)	9.0	grams	S-770
M1166	6.4	grams	**
Antifoam RD	0.25	cc	**
Distilled or softened water to	1.0	liter	

pH: Average pH at 77°f is 11.23. Formulations which have a measured pH outside the range 10.74 - 11.72 should be rejected. Accepted formulations should be pH adjusted to 11.23 $\pm$ 0.10, using 2N Sulfuric Acid or 2N Sodium Hydroxide solution, before being taken into use.

STOP BATH F-16

Tap water	800.0	cc	
Sodium Thiosulfate (anhy.)	109.0	grams	S-810
Sodium Acetate (anhy.)	31.4	grams	S-370
Sodium Sulfite (anhy.)	4.3	grams	S-790
Acetic Acid (glacial)	35.0	cc	**
Potassium Alum	17.0	grams	P-500
Ammonium Chloride	43.0	grams	**
Water to	1.0	liter	

pH: Average pH at 77°f is 4.30. Formulations which have a measured pH outside the range 3.80 - 4.80 should not be taken into use. Accepted formulations should be pH adjusted to 4.30 $\pm$ 0.20, using 2N Sulfuric Acid or 2N Sodium Hydroxide solution, before being taken into use.

REPLENISHER R4 FOR STOP BATH F-16

Tap water	800.0	cc	
Sodium Thiosulfate (anhy.)	147.0	grams	S-810
Sodium Acetate (anhy.)	25.0	grams	S-370
Sodium Sulfite (anhy.)	7.0	grams	S-790
Acetic Acid (glacial)	27.0	cc	**
Potassium Alum	34.0	grams	P-500
Ammonium Chloride	59.0	grams	**
Water to	1.0	liter	

pH: Average pH at 77°f is 4.04. Formulations which have a measured pH outside the range 3.88 - 4.20 should be rejected.

**Not carried by Dignan Photographic, Inc.

BLEACH BATH B-9

			Dignan Catalog Number
Tap water	800.0	cc	
Potassium Ferricyanide	45.0	grams	P-580
Sodium Acetate (anhy.)	9.1	grams	S-370
Potassium Bromide	23.0	grams	P-530
Sodium Nitrate	18.0	grams	**
Potassium Alum	18.0	grams	P-500
Acetic Acid (glacial)	4.0	cc	**
Water to	1.0	liter	

pH: Average pH of this bath at 77°f is 4.25. Formulations which have a measured pH outside the range 4.00 - 4.50 should not be taken into use.

REPLENISHER R3 FOR BLEACH BATH B-9

Tap water	800.0	cc	
Potassium Ferricyanide	75.0	grams	P-580
Sodium Acetate (anhy.)	18.0	grams	S-370
Potassium Bromide	38.0	grams	P-530
Sodium Nitrate	36.0	grams	**
Potassium Alum	36.0	grams	P-500
Acetic Acid (glacial)	8.0	cc	**
Water to	1.0	liter	

pH: Average pH at 77°f is 4.13. Formulations which have a measured pH outside the range 3.86 - 4.40 should be rejected.

FIX BATH F-5

Tap water	800.0	cc	
Sodium Thiosulfate (anhy.)	109.0	grams	S-810
Sodium Acetate (anhy.)	10.2	grams	S-370
Sodium Sulfite (anhy.)	4.3	grams	S-790
Acetic Acid (glacial)	8.5	cc	**
Potassium Alum	17.0	grams	P-500
Ammonium Chloride	43.0	grams	**
Water to	1.0	liter	

pH: Average pH at 77°f is 4.30. Formulations which have a measured pH outside the range 4.09 - 4.51 should be rejected.

REPLENISHER R3 FOR FIX BATH F-5

Tap water	800.0	cc	
Sodium Thiosulfate (anhy.)	164.0	grams	S-810
Sodium Acetate (anhy.)	15.3	grams	S-370
Sodium Sulfite (anhy.)	7.0	grams	S-790
Acetic Acid (glacial)	22.0	cc	**
Potassium Alum	27.0	grams	P-500
Ammonium Chloride	64.0	grams	**
Water to	1.0	liter	

REPLENISHER R3 FOR FIX BATH F-5 - Continued

pH: Average pH at 77°f is 4.00. Formulations which have a measured pH outside the range 3.83 - 4.17 should be rejected.

CONDITIONER BATH C-1

			Dignan Catalog Number
Tap water	800.0	cc	
EDTA Na2	0.50	gram	**
Sodium Carbonate (mono.)	5.3	grams	S-500
Formaldehyde (40% w/v)	10.0	cc	**
8% Lissapol solution*	1.7	cc	**
Water to	1.0	liter	

*Prepare by diluting 80 cc of Lissapol NX, or 300 ml of Lissapol N, to 1 liter.

pH: Average pH at 77°f is 10.50. Formulations which have a measured pH outside the range 10.10 - 10.90 should be rejected. Accepted formulations should be pH adjusted to 10.70 $\pm$ 0.20, using 2N Sulfuric Acid or 2N Sodium Hydroxide solution, before being taken into use.

REPLENISHER R2 FOR CONDITIONER BATH C-1

Tap water	800.0	cc	
EDTA Na2	0.63	gram	**
Sodium Carbonate (mono.)	6.7	grams	S-500
Sodium Hydroxide	2.2	grams	**
Formaldehyde (40% w/v)	11.5	cc	**
8% Lissapol solution*	2.1	cc	**
Water to	1.0	liter	

*Prepare by diluting 80 cc of Lissapol NX, or 300 cc of Lissapol N, to 1 liter.

pH: Average pH at 77°f is 12.15. Formulations which have a measured pH outside the range 11.75 - 12.55 should be rejected. Accepted formulations should be pH adjusted to 12.30 $\pm$ 0.10, using 2N Sulfuric Acid or 2N Sodium Hydroxide solution, before being taken into use.

**Not carried by Dignan Photographic, Inc.